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Synthesis and characterization of composite nanofibers with VARTM and Electrospinning process

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Fiber-reinforced polymer composites have made tremendous advancements in the technology of engineering materials. To manufacture advance composite, quantity and size of reinforcement and failure of the composites play the important role. From various methods of manufacturing composites ,Vacuum Assisted Resin Transfer Molding (VARTM) was found to have high fiber weight fraction which contributes to enhance the mechanical properties of the two phase or three phase nanocomposite, Here we have compared the VATRM and Hand Molding with three different material systems and found the enhanced tensile and flexural strength of two phase composite and manufactured TEOS nanofibers using electrospinning process as secondary reinforcement to improve the interlaminar delamination three phase nanocomposite.

Keywords : Electrospinning, VARTM, Nanofiber, Interlaminar delamination

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Introduction : Nanotechnology has brought revolutionary changes in the properties of the material. The composite materials have dramatically increased, in particular for aerospace, defense and automobiles applications. Specific modulus and high specific strength characteristics of these materials make them attractive in aerospace, automotive, defense and structural applications. High strength, lightweight, continuous fiber reinforced polymer matrix of composites has been a key performance enabler for these platforms. Electrospinning process offers a potential enabling breakthrough to remove the barriers by dramatically reducing fiber diameters resulting in vast improvements in fiber mechanical properties. The diameter of the fibers obtained in the electro spinning process is in the range of 10 nm to 100 nm, which is nearly two to three orders less than that obtained by the conventional spinning process. The reduction in the diameter increases the aspect ratio and the effective surface area of the fibers. These nanofibers with improved properties can be used as secondary reinforcement in composites. Also these nanofibers can have significant enhancement of other properties viz. electronic, optical thermal sensitivity etc and Vacuum Assisted Resin Transfer Molding (VARTM) process as an method to form nanocomposite material.

1. Vacuum Assisted Resin Transfer Molding (VARTM) : In general, composite manufacturing processes have more variations compared to the metal manufacturing processes due to the larger raw material and manufacturing processes variations. Two types of manufacturing techniques, open-molding and closed molding, are typically employed to make composites. open-molding is a relatively simple manufacturing method. However, during the open- molding process, hazardous air pollutants may be emitted. The closed-molding technique is becoming more popular due to its low hazardous emissions [26, 27].Out of the various methods that can be used to manufacture composite laminates ,namely wet lay-up, autoclave processing, filament winding, pultrusion, resin transfer molding(RTM), Vacuum assisted resin transfer molding(VARTM) with some modifications is comparatively simple process and proven useful for testing and research purpose [14, 15]. Figure (1) shows a generalized schematic diagram of the VARTM process. First, the vacuum pump is started on to expel air from the preform assembly. After the system has been equilibrated ,the resin is allowed to flow into the preform. A pressure of 1 atm is maintained to provides driving force for the resin to impregnate the reinforcement and the compression force to compact the preform to the desired fiber volume fraction. The vacuum is left on until the resin has completely gelled. The part may then be cured at room temperature or in an oven [13, 14].

Figure (1) : VARTM processing instrument.

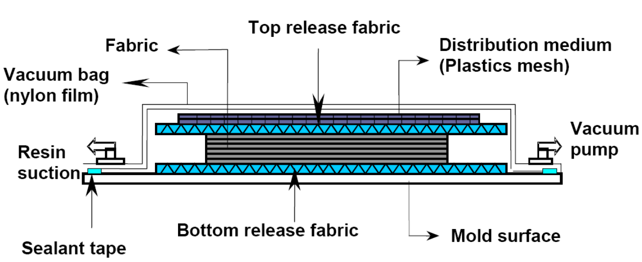

Figure (2) : VARTM setup at BVUCOE, Pune.

FAILURE OF COMPOSITE : One of frequently encountered failure mode of fiber glass composite laminates is interlaminar delamination, which result in an undesirable material failure under mechanical, thermal, or electrical loading.

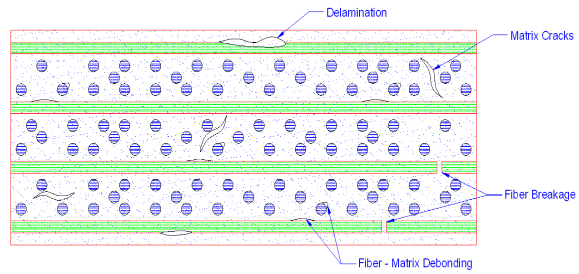

Figure (3) : Various Failure Modes in Composites

A number of methods has been developed to prevent delamination [2 - 5]. These include optimization of stacking sequence, critical ply termination, laminate stitching, edge cap reinforcement, matrix toughening ,braiding and replacement of a stiff ply by one that has softer regions. Above mentioned method are either costly or weight penalties.

A fiber reinforce nanocomposites are the solutions for the delamination ,which are combinations of two materials , one of the materials is called the reinforcing phase which are strong with low densities, is in the form of fibers, sheets, or particles, and are embedded in the other material called the matrix phase is usually a ductile or tough material are further comprising secondary addition of ,small diameter fibers i.e nanofibers manufactured by eletrospinning [7 - 9] or nanoparticle shown in Figure (4) manufactured by hydrothermal, sol–gel, Pechini, chemical vapor deposition, and microwave, Polymerized Complex Method, Chemical Vapor Deposition, High-Energy Ball Milling [28] which can be used for the enhancing the properties of matrix individual or the bond of the matrix and reinforcement, which have increase tensile strength, modulus [10], delamination resistance, Mode I fracture toughness [10]. Enhancement of delamination resistance, stiffness, tensile strength, safety factors was reported for epoxy-based multiscale composites [18]. Mode II Fractures was increased by 45 % and 75 % respectively by doping CFRP with 0.5 % and 1 % [17] Epoxy-silicate nanocomposite using an aerospace grade epoxy resin and carbon fibers and showed higher storage modulus as compared to neat resin properties [19, 20]. Glass fiber/CNT/epoxy nanocomposites shown interlaminar shear strength increased by 20 % [20].

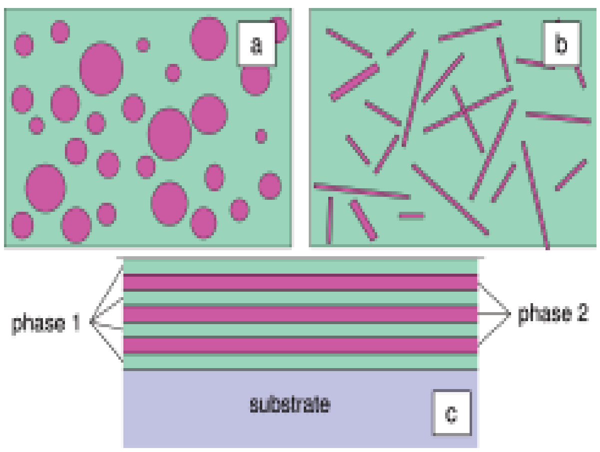

Figure (4) : Three basic types of nanocomposite. (a) Composite consisting of zero-dimensional particles in a matrix; ideally, the individual particles do not touch each other. (b) One-dimensional nanocomposite consisting of nanotubes or nanorods distributed in a second matrix. (c) Two-dimensional nanocomposite built from stacks of thin films made of two or more different materials (Source 25)

Addition of 1 wt. % CNFs reported a 100 % increase in fracture energy of laminates for carbon fiber reinforced epoxy laminates with carbon nanofibers (CNFs) and titanate piezoelectric (PZT) particles [21]. Using Resin Transfer Molding technique (RTM) for fumed silica/glass fiber/epoxy, carbon black/glass fiber/epoxy, and CNT/glass fiber/epoxy micro-nanocomposites reported a 16 % increase in interlaminar shear strength and superior electrical properties [22]. Chowdhury et al. [23] investigated the effects of nanoclay on the mechanical and thermal properties of woven carbon fiber-reinforced epoxy and reported an 18 % and 9 % improvement in flexural strength and modulus, respectively, with the addition of 3 wt. % nanoclay. Woven carbon fiber-reinforced epoxy with the addition of 3 wt. % nanoclay reported an 18 % and 9 % improvement in flexural strength and modulus [23]. Using vacuum-assisted resin transfer molding mechanical properties and electrical conductivity of CFRPs was increased [24].

2. Electrospinning Process

Electrospinning has been identified as the most economic and qualitative process to manufacture nano fibers whose diameter ranges from 10 nm to 100 nm, which is nearly two to three orders less than that obtained by the conventional spinning process [9]. Fibers can be produced drawing, template synthesis, phase separation, self-assembly, extrusion electro spinning. Electrospinning is an efficient method to produce nanofiber from variety of polymer solution. The improvement in electro spinning has been perceived in discussion of reference [6 - 9].

There are basically three parts : (1) A high voltage supplier, (2) A capillary tube with a pipette or needle of small diameter, and (3) Metal collecting screen. One electrode is placed into the polymer solution/melt and the other attached to the metal collector as indicated in Figure (5). The electric field produces surface tension on the polymer, which induces a charge on the surface of the polymer. Further with increasing the electric field, a critical value is attained at which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected in form of polymer nanofiber [9].

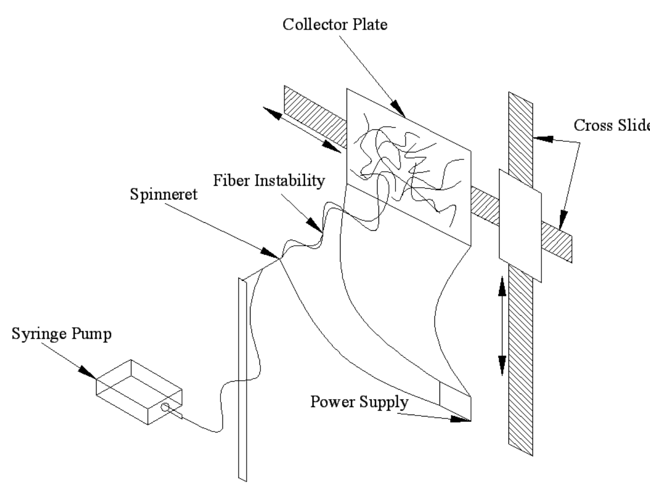

Figure (5) : Schematic for Electrospinning [10].

Figure (6) : Actual Setup for Electrospinning Process at BVUCOE, Pune

Tetra Ethyl Ortho Silicate (TEOS) nanofibers is were manufactured by using Electrospinning. Sol-Gel process is adapted to get the required TEOS solution with suitable stringiness to produce fibers by electro spinning. Electrospinning setup is maintained under controlled ambient conditions of temperature of 72 ^{o}F and humidity of 44 %. Once the fibers are produced, composites are manufactured by impregnating Epon 862 resin into the electrospun fibers restrained in a glass mold. The composites so manufactured are then tested for their mechanical behavior characteristics using a Instron tensile testing setup.

3. Electrospinning Process Parameters :

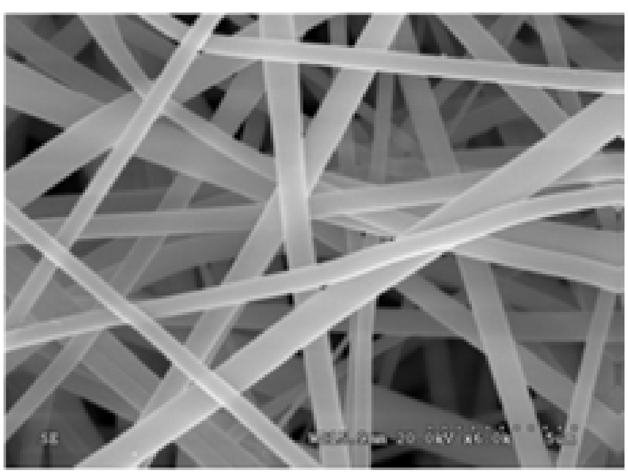

Figure (7) : Setup 1: 15 kV and 70 mm : 669 nm average fiber diameter

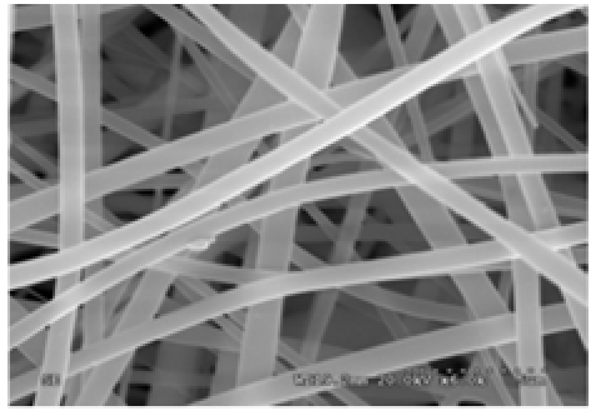

Figure (8) : Setup 2: 15 kV and 100mm. 740 nm average fiber diameter.

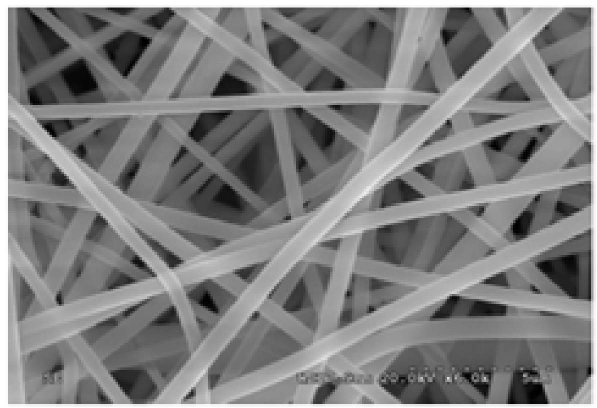

Figure (9) : Setup 3: 18 kV and 70 mm: 515 nm average fiber diameter.

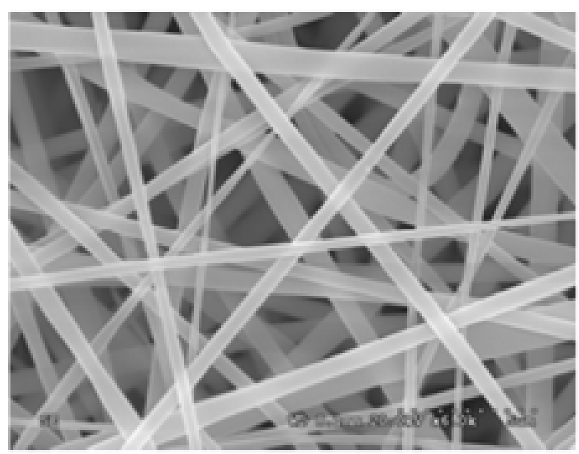

Figure (10) : Setup 4: 18 kV and 100 mm: 665 nm average fiber diameter.

The following figures are the SEM micrographs of the TEOS nanofibers produced by the voltage and throw distance conditions those have been identified to give the minimum diameter.

4. Results and Discussions : Following are the observation with three different material systems and comparison of VARTM with hand molding are shown in the Table (1).

Table (1) : Comparison of VARTM with Hand-molding

	VARTM	**HAND MOULD**	**ASTM Standards**
Material System I Glass fiber and Epoxy (epon 892 and epicure as hardener) 6 Layers			
Tensile strength	422.42 MPa	316 MPa	(D638)
Flexural strength	97.46 MPa	55.56 MPa	(D7264)
Material System II Reinforcement = Triaxial Glass fiber & matrix = Unsaturated Polyester Resin (Roof lite) 6 layers			
Tensile strength	434.27 MPa	358.4 MPa	(D638)
Flexural strength	531.16 MPa	435 MPa	(D7264)
Material System III Reinforcement = Biaxial Glass fiber & matrix = Vinlyester Resin 4 layers			
Tensile strength	273.5 MPa	236 MPa	(D638)

4. Mechanical characterization : Tensile tests were conducted to evaluate the mechanical performance of the composite system (TEOS fibers embedded with Epon 862/W resin). Tensile test were conducted using Instron Model 5500R machine with 1000 N reversible load cell. It was anticipated that there would be an improvement in modulus with tensile strength compared to the neat resin coupons. In second phase of characterization VARTM, was used to manufacture composite panels. Electrospun fibers were impregnated with the EPON 862 resin via VARTM.

Excess amount of resin was removed by applying vacuum over the fiber – resin mixture as in a VARTM setup to get a good fiber volume fraction. The panels so manufactured were then cut into tensile specimens, which were tested using ASTM D648 test standard for composite laminates. The tensile test data obtained from the test coupons is presented in Table (2). The above test data indicates that there has been improvement in the neat resin modulus from 0.68 Msi to 0.83 Msi. This is about 18 % improvement in Modulus compared to the neat resin coupons. However, there is a drop in tensile strength from to 7.22 Ksi to 6.06 Ksi for neat resin coupons.

Specimen No	**Maximum Load (Ksi)**	**Tensile stress at max. load (Ksi)**	**Modulus (Msi)**
Sample With Nanofiber 1	0.13	5.94	0.79
Sample With Nanofiber 2	0.13	5.08	0.74
Sample With Nanofiber 3	0.20	6.28	0.85
Sample With Nanofiber 4	0.16	6.96	0.97
		6.06	**0.83**
Sample With Microfiber 1	0.19	8.54	0.68
Sample With Microfiber 2	0.17	8.09	0.73
Sample With Microfiber 3	0.22	4.54	0.77
Sample With Microfiber 4	0.15	7.73	0.57
		7.22	**0.68**

6. Conclusions : We conclude that -

(1) VARTM process has shown enhancement of tensile and flexural properties comparable to the hand molding.

(2) TEOS fibers with minimum diameter are produced with two extreme values of voltage and distance between spinneret and grounded collector.

(3) There is improvement in the modulus of two phase composite consisting of Epon 862 resin and electrospun TEOS nanofibers.

(4) Future studies will focus on the performance of electrospun sheets of different material and modified VARTM process for produced at optimized diameter of nanofiber and tensile strength of two phase composite.

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